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# Thermal effects in exciton harvesting in biased one-dimensional systems

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## Abstract

The study of energy harvesting in chain-like structures is important due to its relevance to a variety of interesting physical systems. Harvesting is understood as the combination of exciton transport through intra-band exciton relaxation (via scattering on phonon modes) and subsequent quenching by a trap. Recently, we have shown that in the low temperature limit different harvesting scenarios as a function of the applied bias strength (magnitude of the energy gradient towards the trap) are possible [S.M. Vlaming, V.A. Malyshev, J. Knoester, *J. Chem. Phys.* 127 (2007) 154719]. This paper generalizes the results for both homogeneous and disordered chains to nonzero temperatures. We show that thermal effects are appreciable only for low bias strengths, particularly so in disordered systems, and lead to faster harvesting.

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## 1. Introduction

The study of energy transport and trapping in molecular scale systems is an interesting topic, because of its relevance to natural systems (photosynthetic antenna complexes [1]) and applications in nanophysics and quantum computing, where energy should efficiently be transported over some distance. Linear molecular aggregates [2,3], conjugated polymers [4,5], photonic wires [6,7] and quantum dot arrays [8,9] may all be envisioned as realizations of such energy transport complexes. A natural question that arises is how this combined process of transport and eventual trapping, which we will from now on refer to as harvesting, can be optimized. In a previous paper [10], we performed a study on the effect of an energy gradient (bias) on the energy harvesting properties of a linear system. The scope there was limited to low temperatures. In this paper, we present numerical calculations of thermal effects on the harvesting time and a qualitative analysis of the results.

## 2. Model

We use a Frenkel exciton model to describe the excited state dynamics in chain-like systems. The latter are modeled as a regular one-dimensional array of two-level monomers that are coupled through their transition dipole moments, which are assumed to be oriented parallel to each other. We initially excite a monomer at one end of the chain ( $n = N$ ), and consider the other end ( $n = 1$ ) as a trap. The harvesting time is calculated as the average time it takes for an excitation to move across the chain and to be quenched by the trap. Including diagonal disorder and a bias ( $\Delta > 0$ ) towards the trap, the model Hamiltonian reads

$$H_{\text{ex}} = \sum_{n=1}^N [\varepsilon_n + (n-1)\Delta] |n\rangle \langle n| + \sum_{n,m \neq n}^N J_{nm} |n\rangle \langle m|, \quad (1)$$

where the state  $|n\rangle$  denotes that monomer  $n$  is excited while all other monomers are not, the excitation energies  $\varepsilon_n$  are uncorrelated Gaussian stochastic variables with zero mean and standard deviation  $\sigma$  and the transfer integrals are  $J_{nm} = -J/|n-m|^3$ , with the nearest-neighbor coupling  $J > 0$ . Diagonalization of this Hamiltonian yields collective excited states,  $|s\rangle = \sum_n c_{sn} |n\rangle$ , where the site amplitudes can be chosen real. Both a bias and disorder result in

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localization of the states, Bloch-like [11] and Anderson-like [12], respectively, so that the exciton states are spread out over finite segments of the chain only. In the case of a bias, there exists a correlation between the location of the eigenstate and its energy, as lower energy states are located in the vicinity of the trap.

The dynamics of the populations  $P_s$  of the various exciton states is analyzed within the framework of the Pauli master equation,

$$\dot{P}_s = -(\gamma_s + \Gamma_s)P_s + \sum_{s'} (W_{ss'}P_{s'} - W_{s's}P_s), \quad (2)$$

where  $\gamma_s = \gamma_0(\sum_n c_{sn})^2$  is the radiative rate of the state  $|s\rangle$  ( $\gamma_0$  being the radiative rate of a monomer) and  $\Gamma_s$  is the quenching rate, which is taken proportional to the exciton probability at the trap ( $n=1$ ):  $\Gamma_s = \Gamma c_{s1}^2$  where  $\Gamma$  is the quenching amplitude [13], which cannot be arbitrarily large within the limitations of our model [10]. As at  $t=0$  only the rightmost site  $n=N$  is excited, the initial population distribution is given by  $P_s(0) = c_{sN}^2$ . The  $W_{ss'}$  describe the scattering of population between various exciton states through interaction with phonons:  $W_{ss'} = W_0 S(E_s - E_{s'}) \sum_{n=1}^N c_{sn}^2 c_{s'n}^2 G(E_s - E_{s'})$ , where  $W_0$  is the scattering amplitude,  $S(E)$  is the phonon spectral density function,  $\sum_{n=1}^N c_{sn}^2 c_{s'n}^2$  is the probability overlap, and  $G(E) = 1 + n(E)$  if  $E < 0$ , while  $G(E) = n(E)$  if  $E > 0$  with  $n(E) = [\exp(|E|/T) - 1]^{-1}$  the phonon occupation factor. We use a Debye-like spectral density with cut-off  $\omega_c$ ,  $S(E) = |E/J|^3 \exp(-|E|/\omega_c)$ . The harvesting time is defined as follows:  $\tau^{-1} = \tau_{\text{trap}}^{-1} - \tau_0^{-1}$ , where  $\tau_{\text{trap}}$  and  $\tau_0$  are the decay times with and without trap, respectively. They are calculated as  $\int_0^\infty dt \langle \sum_s P_s(t) \rangle$ , where  $\langle \dots \rangle$  denotes the disorder average.

### 3. Disorder-free biased chains

We begin with a discussion of the harvesting efficiency in homogeneous chains ( $\sigma=0$ ). The bias-induced Bloch localization dramatically changes the harvesting properties. Depending on the relative strengths of the quenching and relaxation processes, both monotonic decreasing and nonmonotonic behavior of the harvesting time as a function of the bias strength can be obtained. We refer to our earlier paper [10] for a full discussion of the possible scenarios, while here we focus on the aspects relevant to understanding thermal effects in our model.

In the limit of  $\Gamma \ll W_0$  and for low temperature, relaxation to lower exciton states is the dominant process for virtually all exciton states. As a result, most population ends up in the bottom states of the band. For zero bias, the quenching rate from these states is low because of the poor overlap of the bottom states with the trap (see Fig. 1). However, turning on the bias increases this overlap, thereby accelerating the harvesting process. Temperature will enhance the harvesting efficiency at low bias by shifting population from the poorly quenched bottom state(s) to more strongly quenched higher energy states. This en-

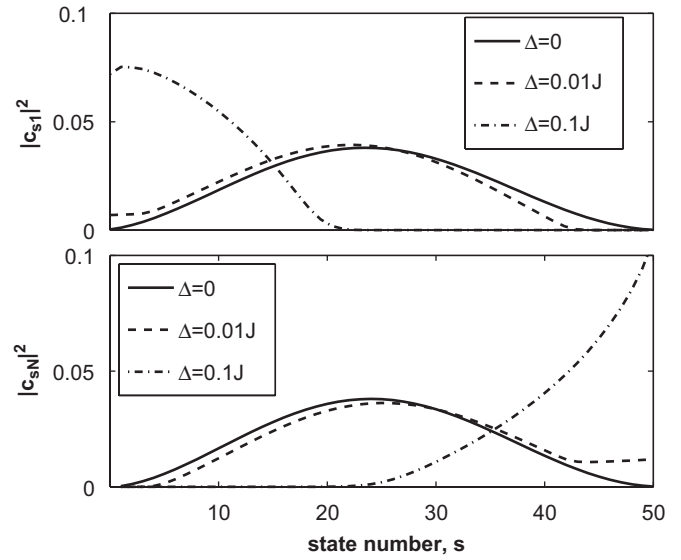


Fig. 1. Bias dependence of the exciton probabilities  $c_{sN}^2$  and  $c_{s1}^2$  that determine the initial distribution of the exciton population  $P_s(0)$  and the quenching rate  $\Gamma_s$ , respectively, for chains without disorder ( $\sigma=0$ ). The bias tends to shift the initial distribution of population to the top of the band (to higher  $s$ ). Oppositely, the strongly quenched states occur at the lower band edge (for small  $s$ ).

hancement disappears for higher bias strengths, as the higher energy states are no longer more strongly quenched than the bottom states, as is shown in Fig. 2(a).

The interesting situation where  $\Gamma \sim W_0$  provides a nonmonotonic bias dependency of  $\tau$ . A small bias is advantageous for the harvesting process as it increases the quenching rate for the bottom states, but beyond some optimal bias value the increase in relaxation time overtakes the previous effect in importance and the net effect of increasing the bias becomes negative. The thermally induced changes in the harvesting efficiency are again only present for small values of the bias, for the reasons mentioned in the discussion of the limit of  $\Gamma \ll W_0$ . This is corroborated in Fig. 2(b).

In the limit  $\Gamma \gg W_0$  our model does not adequately describe the harvesting, in particular when the exciton states are delocalized over the entire chain (i.e., small bias, small disorder, and relatively short chains). In this situation, the off-diagonal density matrix elements (exciton coherences), which are also created by populating the site  $n=N$  ( $\rho_{ss'}(0) = c_{sN}c_{s'N}$ ), are sufficiently long-lived to be relevant to the transport process. In fact, neglecting coherences leads to the unphysical artifact that there is instantaneous energy transfer over the chain. A more refined approach is necessary to remove the occurrence of unphysically fast energy transfer; we refer to our earlier paper [10] for a more detailed discussion of this limit and its complications.

### 4. Disordered biased chains

The inclusion of disorder slows down the energy transport process for all bias values; however, the effect

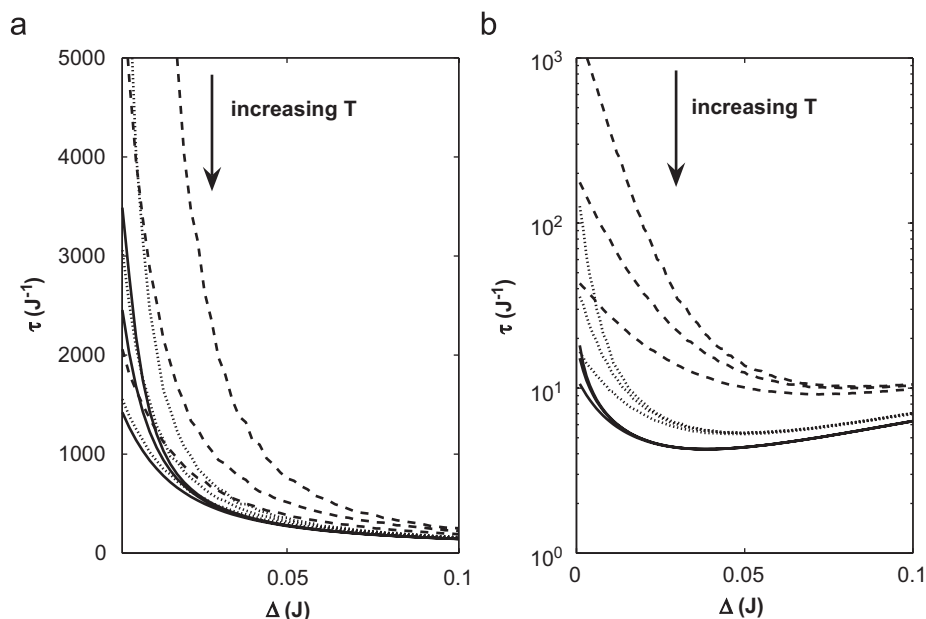


Fig. 2. Harvesting time  $\tau$  versus the applied bias magnitude  $\Delta$  calculated for disordered chains of 50 sites for the quenching amplitude  $\Gamma = 10^{-1}J$  (panel (a)) and  $\Gamma = 10J$  (panel (b)) and the scattering amplitude  $W_0 = 10J$ . The curves were calculated for different temperatures,  $T = 0.02J$ ,  $0.2J$  and  $0.4J$ , which are ordered as shown by the arrow. Solid, dotted and dashed curves correspond to disorder strength  $\sigma = 0$ ,  $0.2J$  and  $0.4J$ , respectively.

is especially strong for small biases. This will lead to a shift of the optimal bias (when  $W_0 \sim \Gamma$ ) to higher values with increasing disorder strength. The overall shape of the  $\tau(\Delta)$  curve does not change in most cases: only in the case of a high quenching amplitude Fig. 2(b), we see that an optimal bias appears as a result of the fact that the disorder does more damage for low biases than for higher ones.

The explanation of these effects is straightforward. Disorder results in Anderson localization, even in the absence of a bias. This leads to reduced relaxation rates, since the overlap of different states decreases. The effect is particularly significant for systems with a low bias, since in a disorder-free chain the excitons are then delocalized over the whole chain. For higher biases, there is already considerable localization because of the bias itself, and the effect produced by the disorder is relatively small. More importantly, for sufficiently strong disorder and small bias the lowest energy states are not necessarily located near the trap. At low temperatures, a large population is built up in these states and the excitation may thus be unable to be trapped efficiently because of the blockage of diffusion [13,14]. A bias forces these low energy states to be located near the trap and thus accelerates the harvesting.

Thermal effects are marginal for large bias strengths. In this case, the harvesting process consists largely of downward relaxation followed by quenching from the bottom states. These states tend to be localized near the trap and the quenching process is therefore hardly accelerated by thermally induced population shifts to higher energy states. In contrast, the thermal effects for small bias are quite strong in disordered systems, even more so than in homogeneous chains. As has been noted in the previous paragraphs, population tends to end up in the exciton

states at the bottom of the band. These, in general, are not located near the trap and thus are quenched poorly. Increasing the temperature has two effects. First, it rapidly accelerates the exciton diffusion, and second, the population is thermally excited to higher energy states, which are quenched more strongly due to a better overlap with the trap. In other words, the interaction of excitons with the phonon bath can counteract some of the detrimental effects of Anderson localization on the harvesting process, as can be seen in Fig. 2.

## 5. Conclusions

Contrary to what one might naively expect, namely that an energetic bias towards the trap will decrease the harvesting time, we have shown that various scenarios are possible, depending on the relative strengths of the relevant subprocesses. This is already apparent in low temperature systems (with and without disorder) [10], and the same holds for systems at elevated temperature. Thermal effects are only significant for small bias strengths and tend to accelerate harvesting, especially in disordered systems.

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